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GIXRF–NEXAFS investigations on buried ZnO/Si interfaces: A first insight in changes of chemical states due to annealing of the specimen

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ABSTRACT

GIXRF–NEXAFS is a combination of X-ray spectroscopy methods which allows for a non-destructive, depth-dependant chemical speciation of layer systems in the range of a few to several hundred nanometers. We applied this technique to a model system for thin-film silicon solar cells, a Si/ZnO layer system, which was investigated in its as-deposited and its annealed state. By means of total reflection at the buried ZnO/Si interface we could gain access to chemical information on the interface. In addition, a diffusion of contaminants from the ZnO into the Si was observed after annealing.

1. Introduction

Thin-film stacks comprising ZnO and Si films are basic building blocks of various promising thin-film solar cell concepts. In these stacks the electronic quality of the ZnO/Si interfaces critically affects solar cell performance. In case of polycrystalline silicon (poly-Si) films which are formed on ZnO at temperatures above 600 °C the control of the ZnO/Si interface becomes especially crucial. Through the high temperature, chemical reactions at the interface and diffusion of impurities into the various layers may modify the electronic properties of this layer stack that serves as an important ingredient of new types of thin-film solar cells [1]. To study this in detail, we present a novel approach to characterize such buried ZnO/Si interfaces by means of monochromatized synchrotron radiation.

We applied grazing incidence X-ray fluorescence combined with near edge X-ray absorption fine structure spectroscopy (GIXRF–NEXAFS) [2] at the PGM- and the FCM-beamline in the PTB laboratory at BESSY II to gain access to the chemical state and elemental distribution of the buried ZnO/Si interface. In order to show the effectiveness of such an approach we investigated well characterized model systems in an as-deposited state as well as after annealing. The question for the analysis was to determine differences at the ZnO/Si interface between the annealed and as-deposited sample.

2. Sample system and treatment

The structure of the sample system is shown in Fig. 1. An 80 nm SiN layer acts as a barrier preventing the diffusion of contaminants from the Borofloat glass substrate into the silicon during high-temperature treatments. The ZnO:Al films of 900 nm thickness were deposited at a temperature of 300 °C by non-reactive RF magnetron sputtering from ceramic ZnO targets containing 1 wt% Al2O3 [3]. The ZnO:Al is covered by a 50 nm thick highly phosphorous doped amorphous silicon (a-Si:H(P)) layer by plasma-enhanced chemical vapour deposition (PECVD) at 210 °C. Two samples were produced out of one batch: One is kept in the as-deposited – amorphous – state and one was annealed at 600 °C for 72 h, so that the a-Si:H(P) layer is completely crystallized.

For GIXRF measurements roughness plays an important role, therefore the samples were pre-examined with a profilometer. The rms-roughness was around 3 nm for the as-deposited and around 5 nm for the annealed sample, respectively, thus allowing for external total reflection of X-rays in certain photon energy ranges. Additionally, an overall curvature (8 mm line scan) of the

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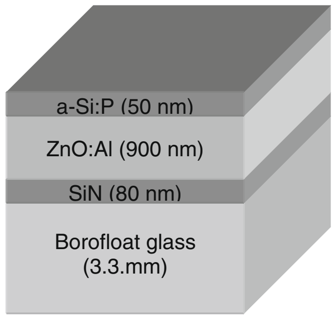

Fig. 1. Layer stack consisting of a-Si:H (0.2 at.% P), ZnO (1 wt% Al_2O_3), and SiN. The layer stack is deposited on Borofloat glass.

samples was observed which is less than 0.1 μm for the as-deposited and about 4.0 μm for the annealed one. The higher curvature of the annealed sample can be explained by stress that emerges during annealing of the sample.

For the X-ray measurements only the two top layers were relevant for the investigated angular range.

3. Methodological

The samples were investigated by a combination of X-ray fluorescence analysis (XRF) and near edge X-ray absorption fine structure spectroscopy (NEXAFS) under grazing incidence (GI) conditions. The latter ensures the analytical sensitivity and depth profiling capability of the method in the nanometer regime. With XRF the elemental composition of a sample can be non-destructively determined, whereas with NEXAFS chemical speciation can be derived. Combining both methods requires NEXAFS to be carried out in fluorescence mode, i.e. detecting an element-specific fluorescence line by tuning the excitation energy around the absorption edge of the specific elemental ionisation shell. Hence, GIXRF–NEXAFS offers a non-destructive access to depth-resolving analysis of buried nanolayers with respect to both the chemical speciation and the layer composition. By varying the angle of incidence, the penetration depth can be tuned from a few to several hundreds nanometers. Probing of a buried interface is done by total reflection of the incident radiation at this boundary layer, see Fig. 2. The incident and reflected beam are forming a standing wave field (XSW) which nodes probe the Si layer when the angle of incidence is varied, hence modulations of the Si signal can be seen in Fig. 4.

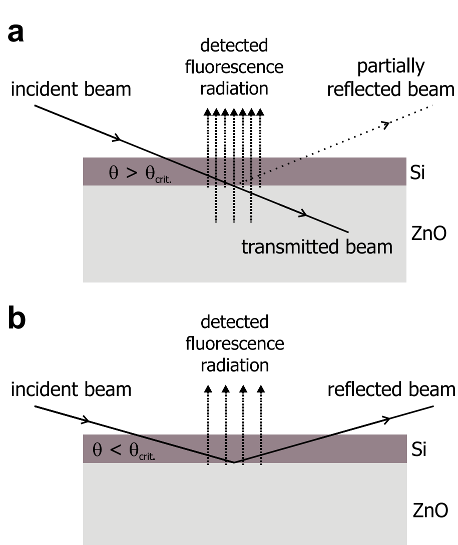

Fig. 2. Conditions for total reflection at a buried layer. If the angle of the incident beam is higher than the critical angle of total reflection of the top layer (i.e. Si) the beam penetrates the first layer. (a) If the incident angle is still higher than the critical angle for the buried layer (i.e. ZnO) the beam propagates into the second layer as well, fluorescence is detected from both layers. (b) If the angle is lower than the critical angle for the buried layer the beam will be reflected at the interface, hence fluorescence is only detected from the first layer and the interface.

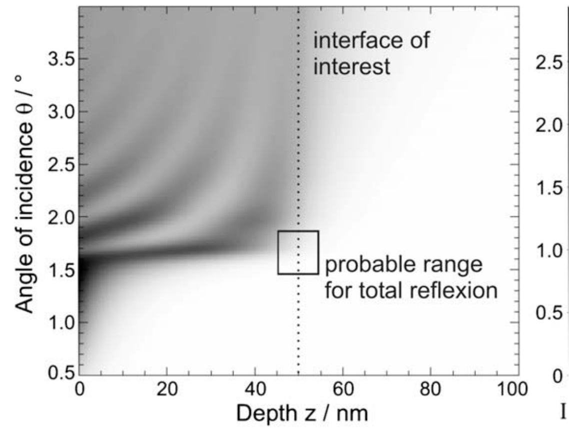

Fig. 3. Simulation of the relative XSW intensity I for an incident energy of 1060 eV (just above the Zn $L_{III,II}$-edges) with varying incident angle. For an angle of 1.7 (±0.2)° a region of possible total reflection at the buried ZnO layer can be seen.

First measurements were performed to test the sensitivity of GIXRF–NEXAFS for the Zn K- and L-edge regions of the buried Si/ZnO interface. To gain information from the interface, the mean X-ray penetration depth into the ZnO layer was set to less than 10 nm by an appropriate choice of the incident angle. This angle was calculated with IMD [4], which revealed an angular region of possible total reflection at this interface (see Fig. 3).

4. IMD simulations

IMD is a software which allows to calculate optical properties of multilayer systems [4]. In this work we used it for simulations of the propagation of the electric field of the incident radiation into the Si and ZnO layer.

Fig. 3 shows the simulation of the standing wave field intensity for an incident energy of 1060 eV (just above the Zn $L_{III,II}$-edges) with varying incident angle. Below the critical angle of Si (<0.5°) the incident radiation is reflected. For increasing angles the radiation is starting to penetrate the Si layer but not the ZnO layer since the critical angle for ZnO is higher than for Si. That is why for an angle of 1.7° (±0.2)° a region of possible total reflection at the buried interface can be seen which renders this method sensitive for the interface if an elemental contribution is probed that is not present in the cap layer. Otherwise, it is not possible to gain direct access to the interface. Similar calculations were carried out for incident energy of 10 keV which is just above the Zn K-edge. These calculations also show total reflection at the buried interface for angles of 0.21° (±0.03)° (not shown here).

Since roughness plays an important role for the reflectance it has to be taken into account in the simulations. The estimated roughness of 5 nm for the annealed and 3 nm for the as-deposited sample appeared to be low enough for maintaining total reflection in the experiments according to the simulations.

5. GIXRF measurements

In order to define the appropriate incident angle for total reflection at the buried interface, X-ray fluorescence measurements